

Hylleraas-Configuration Interaction calculations on helium atom

María Belén Ruiz*

Department of Theoretical Chemistry

Friederich-Alexander-University Erlangen-Nürnberg,

Egerlandstraße 3, 91058 Erlangen, Germany

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Abstract

Hylleraas-Configuration Interaction (Hy-CI) calculations on the ground 1S state of helium atom are presented using s -, p -, and d -Slater orbitals of both real and complex type. Techniques of construction of adapted configurations, optimization of the orbital exponents, structure of the wave function expansion are explored. A new method to evaluate the two-electron kinetic energy integrals occurring in the Hy-CI method is presented. The calculations show that nanohartree accuracy, about 0.0002cm^{-1} is achieved.

*E-mail address: Maria.Belen.Ruiz@chemie.uni-erlangen.de

1. Introduction

The Configuration Interaction method (CI) is of great importance in quantum mechanical calculations of the electron structure of atoms and molecules. It is well known that the shortcomings of the CI method are due to the form of the wave function which does not fulfill the electronic cusp condition [1]:

$$\left(\frac{1}{\Psi} \frac{\partial \Psi}{\partial r_{ij}} \right)_{r_{ij}=0} = \frac{1}{2}. \quad (1)$$

The CI wave function does not contain explicitly odd powers of the interelectronic coordinate r_{ij} (implicitly the CI wave function does contain terms $r_{ij}^2, r_{ij}^4, \dots, r_{ij}^{2n}$ formed by combination of angular orbitals p, d, f [2–4]). But odd powers are the ones energetically important [5]. In the CI wave function the piling up of higher and higher angular terms attempting to represent the term r_{ij} like in a Taylor expansion [5] shows how important the details of the cusp are. The energy improvement when increasing the quantum number l follows an asymptotic formula proportional to $(l+1/2)^{-4}$ [6] in the case of helium atom, and in general for a larger number of electrons [7, 8]. The nuclear cusp condition is always fulfilled, in the CI as in the Hartree-Fock (HF) wave functions:

$$\left(\frac{1}{\Psi} \frac{\partial \Psi}{\partial r_i} \right)_{r_i=0} = -Z, \quad (2)$$

Z is the atomic charge, or the orbital exponent. The cusps (positive for repulsion and negative for attraction) account for two-body correlation, but not for three-body correlation.

These conditions are a result of the singularities of the Hamiltonian at $r_i = 0$ and $r_{ij} = 0$:

$$H = -\frac{1}{2} \sum_{i=1}^2 \frac{\partial^2}{\partial r_i^2} - \sum_{i=1}^2 \frac{1}{r_i} \frac{\partial}{\partial r_i} - \sum_{i=1}^2 \frac{2}{r_i} + \frac{1}{r_{12}} - \frac{2}{r_{12}} \frac{\partial}{\partial r_{12}} - \frac{1}{2} \sum_{i \neq j}^2 \frac{r_i^2 + r_{12}^2 - r_j^2}{r_i r_{12}} \frac{\partial^2}{\partial r_i \partial r_{12}}. \quad (3)$$

As the exact wave function is obtained from the equation: $H\Psi/\Psi = E$. This equation leads to the exact energy only if the cusps conditions of Eqs. (1,2) are fulfilled. The CI wave function is then not a formal solution of the Schrödinger equation and therefore the CI wave function converges very slowly. Schwartz [9] has demonstrated that the inclusion of other terms than r_{12} into the wave function, like negative powers of r_i [10], fractionary powers of r_i [11] and logarithmic terms $\ln(r_i + r_j)$ accelerates the convergence of the wave

function to the exact solution. Logarithmic terms are important to describe the three-particle coalescence region [12, 13]. Nakatsuji [14] has proposed the Iterative-Complement-Interaction (ICI) method which generates those terms which are necessary in the structure of the wave function for very highly accurate calculations. Including a $\ln(r_1 + r_2 + \beta r_{12})$ in the wave function a 40 decimal digits accurate energy was calculated, showing that logarithmic terms are necessary. Such accurate calculations are restricted to the case of two-electron systems.

Other of the shortcomings of the CI wave function are the functions used as orbitals. If the functions form a complete set it is obvious that the exact solution can be expressed in terms these functions. Some types of orbitals form a complete set (or overcomplete in case of double basis) like Slater orbitals and Sturmians. If the set is not complete the wave function needs some states from the continuum. The importance the continuum functions in representing the ground state of helium atom has been pointed out by many authors [15, 16]. If one carries out calculations to the ultimative limit it is immaterial which set is used. Therefore an infinite expansion of CI configurations would be the exact wave function. The reason why the CI wave function gives good results is the consecutive inclusion of angular functions which represent r_{ij} .

It is then clear that the explicit correlated wave functions including the interelectronic coordinate r_{ij} proposed by Hylleraas [17] are an alternative to the CI wave function. Sims and Hagstrom [18, 19] introduced the Hylleraas-Configuration Interaction (Hy-CI) wave function which combines the use of higher angular momentum orbitals as CI does with the inclusion of the interelectronic distance into the wave function as the Hylleraas-type wave functions. The first terms of a Hylleraas-CI wave function are CI terms.

Helium atom has been subject of numerous investigations. Its electronic structure has been determined to the greatest accuracy known in quantum chemistry. Our interest is to test in the case of helium atom our integral subroutines and computational techniques as the spin, antisymmetrization, construction of symmetry adapted configurations, the usage of the Hamiltonian in Hylleraas coordinates, and to win experience to investigate larger systems.

This work will be thoroughly referred and compared first, to the early helium calculation of Weiss [5] for which there is enough computational data, and second, to the highly accurate more modern Configuration Interaction and Hylleraas-Configuration Interaction (Hy-CI)

calculations of Sims and Hagstrom [3]. The CI calculation of Weiss is taken as starting point to check our program code. The CI and Hy-CI calculations of Sims and Hagstrom have been taken for comparison as the s,p,d-limits. Finally we have reproduced Hy-CI calculations of Sims and Hagstrom [20].

Novel in this work is the use of a different technique to evaluate the kinetic energy Hy-CI integrals which we have used to reproduce the energy values obtained from Sims and Hagstrom.

2. The Hylleraas-CI wave function

The Hy-CI wave function [19] for the 1S ground state of helium atom is written:

$$\Psi = \sum_{k=1}^N C_k \Phi_k, \quad \Phi_k = \hat{O}(L^2) \hat{\mathcal{A}} \psi_k \chi, \quad \chi = (\alpha\beta - \beta\alpha), \quad (4)$$

where Φ_k are symmetry adapted configurations, N is the number of configurations and the constants C_k are determined variationally. The operator $\hat{O}(L^2)$ projects over the proper spatial space, so that every configuration is eigenfunction of \hat{L}^2 . $\hat{\mathcal{A}}$ is the 2-particle antisymmetrization operator, and χ is the spin eigenfunction. The Hartree products ψ_k , are products of orbitals of the required symmetry multiplied by the interelectronic coordinate:

$$\psi_k = \phi_{ik}(1) \phi_{ik}(2) r_{12}^\nu, \quad \nu = 0, 1 \quad (5)$$

For $\nu = 0$ the Hylleraas-CI wave function reduces to the CI wave function. The power $\nu = 1$ does not represent any restriction. As discussed in Refs. [2, 21, 22], we know that even powers of the interelectronic coordinate are equivalent to products of p -, d -, \dots type orbitals, for instance:

$$r_{12}^2 \equiv p(1)p(2). \quad (6)$$

Furthermore, higher odd powers can be expressed as $r_{12} r_{12}^{2n}$. It can be demonstrated [21] that r_{12} is an infinite expansion of angular orbitals:

$$s(1)s(2)r_{12} \equiv s(1)s(2) + p(1)p(2) + d(1)d(2) + f(1)f(2) + \dots \quad (7)$$

In the case of two-electrons systems Sims and Hagstrom [3] have shown that the Hy and Hy-CI wave functions are equivalent.

3. The Hamiltonian

For a Hy-CI wave function in helium atom the effective Hamiltonian in Hylleraas coordinates may be written[35] [23]:

$$\begin{aligned} \hat{H} = & -\frac{1}{2} \sum_{i=1}^2 \frac{\partial^2}{\partial r_i^2} - \sum_{i=1}^2 \frac{1}{r_i} \frac{\partial}{\partial r_i} - \sum_{i=1}^2 \frac{2}{r_i} + \frac{1}{r_{12}} - \frac{2}{r_{12}} \frac{\partial}{\partial r_{12}} - \frac{1}{2} \sum_{i \neq j}^2 \frac{r_i^2 + r_{12}^2 - r_j^2}{r_i r_{12}} \frac{\partial^2}{\partial r_i \partial r_{12}} \\ & - \frac{1}{2} \sum_{i=1}^2 \frac{1}{r_i^2} \frac{\partial^2}{\partial \theta_i^2} - \frac{1}{2} \sum_{i=1}^2 \frac{1}{r_i^2 \sin^2 \theta_i} \frac{\partial^2}{\partial \varphi_i^2} - \frac{1}{2} \sum_{i=1}^2 \frac{\cot \theta_i}{r_i^2} \frac{\partial}{\partial \theta_i} \\ & - \sum_{i \neq j}^2 \left(\frac{r_j}{r_i r_{12}} \frac{\cos \theta_j}{\sin \theta_i} + \frac{1}{2} \cot \theta_i \frac{r_{12}^2 - r_i^2 - r_j^2}{r_i^2 r_{12}} \right) \frac{\partial^2}{\partial \theta_i \partial r_{12}} - \sum_{i \neq j}^2 \frac{r_j}{r_i r_{12}} \frac{\sin \theta_j}{\sin \theta_i} \sin(\varphi_i - \varphi_j) \frac{\partial^2}{\partial \varphi_i \partial r_{12}}. \end{aligned} \quad (8)$$

Using the Hamiltonian in this form is easy to derive the involved integrals. The angular momentum operator can be extracted and its eigenvalue equation used:

$$\sum_{i=1}^2 \frac{1}{r_i^2} \hat{L}_i^2 = -\frac{1}{2} \sum_{i=1}^2 \frac{1}{r_i^2} \frac{\partial^2}{\partial \theta_i^2} - \frac{1}{2} \sum_{i=1}^2 \frac{1}{r_i^2 \sin^2 \theta_i} \frac{\partial^2}{\partial \varphi_i^2} - \frac{1}{2} \sum_{i=1}^2 \frac{\cot \theta_i}{r_i^2} \frac{\partial}{\partial \theta_i}, \quad (9)$$

$$L_i^2 \phi_i = l_i(l_i + 1) \phi_i, \quad (10)$$

with l_i the angular quantum number of the orbital ϕ_i .

From the variational principle one obtains the matrix eigenvalue problem:

$$(\mathbf{H} - E\mathbf{\Delta})\mathbf{C} = \mathbf{0},$$

where the matrix elements are:

$$H_{kl} = \int \Phi_k H \Phi_l d\tau, \quad (11)$$

$$\Delta_{kl} = \int \Phi_k \Phi_l d\tau. \quad (12)$$

4. The use of real Slater orbitals

We have constructed a set of real s -, p -, d -Slater orbitals which are orthogonal and unnormalized. The exponents are considered as adjustable parameters. They are defined as:

$$\begin{aligned}
ns &= r^{n-1} e^{-\alpha r} \\
np_z &= r^{n-1} e^{-\beta r} \cos(\theta) \\
np_x &= r^{n-1} e^{-\beta r} \sin(\theta) \cos(\varphi) \\
np_y &= r^{n-1} e^{-\beta r} \sin(\theta) \sin(\varphi) \\
nd_{z^2} &= r^{n-1} e^{-\gamma r} \left(\frac{3}{2} \cos^2(\theta) - \frac{1}{2} \right) \\
nd_{xz} &= r^{n-1} e^{-\gamma r} \sin(\theta) \cos(\theta) \cos(\varphi) \\
nd_{yz} &= r^{n-1} e^{-\gamma r} \sin(\theta) \cos(\theta) \sin(\varphi) \\
nd_{xy} &= r^{n-1} e^{-\gamma r} \sin^2(\theta) \cos(\varphi) \sin(\varphi) \\
nd_{x^2-y^2} &= r^{n-1} e^{-\gamma r} \sin^2(\theta) (\cos^2(\varphi) - \sin^2(\varphi))
\end{aligned} \tag{13}$$

The orbitals are eigenfunctions of \hat{L}^2 , but they are not eigenfunctions of \hat{L}_z .

4.1 CI Integrals over real Slater orbitals

The evaluation of the resulting matrix elements Eq. (11) for a CI wave function leads to products of one- and two-electron integrals. These integrals can be evaluated as shown in [24], we write here compact expression of all non-vanishing two-electron integrals[36] over p -orbitals:

$$\begin{aligned}
\langle s(1)s(2)\frac{1}{r_{12}}s(1)s(2)\rangle &= (4\pi)^2\left\langle\frac{1}{g_{12}}\right\rangle, \\
\langle s(1)p_i(2)\frac{1}{r_{12}}s(1)p_i(2)\rangle &= \frac{(4\pi)^2}{3}\left\langle\frac{1}{g_{12}}\right\rangle, \quad i = x, y, z \\
\langle p_i(1)s(2)\frac{1}{r_{12}}s(1)p_i(2)\rangle &= \frac{(4\pi)^2}{9}\left\langle\frac{s_{12}}{g_{12}^2}\right\rangle, \quad i = x, y, z \\
\langle p_i(1)p_i(2)\frac{1}{r_{12}}p_i(1)p_i(2)\rangle &= (4\pi)^2\left\langle\frac{1}{9}\frac{1}{g_{12}} + \frac{4}{225}\frac{s_{12}^2}{g_{12}^3}\right\rangle, \quad i = x, y, z \\
\langle p_i(1)p_j(2)\frac{1}{r_{12}}p_i(1)p_j(2)\rangle &= (4\pi)^2\left\langle\frac{1}{9}\frac{1}{g_{12}} - \frac{2}{225}\frac{s_{12}^2}{g_{12}^3}\right\rangle, \quad i \neq j, \quad i, j = x, y, z \\
\langle p_i(1)p_j(2)\frac{1}{r_{12}}p_j(1)p_i(2)\rangle &= (4\pi)^2\left\langle\frac{1}{75}\frac{s_{12}^2}{g_{12}^3}\right\rangle, \quad i \neq j, \quad i, j = x, y, z
\end{aligned} \tag{14}$$

where s_{12} is the smallest of r_1 and r_2 , and g_{12} the largest of r_1 and r_2 . The radial part of these integrals is expanded in terms of auxiliary integrals [24]. The non-vanishing integrals including d -orbitals are:

$$\langle s(1)d_{iz}(2)\frac{1}{r_{12}}s(1)d_{iz}(2)\rangle = \frac{(4\pi)^2}{75}\left\langle\frac{s_{12}^2}{g_{12}^3}\right\rangle, \quad i = x, y \quad (15)$$

$$\langle s(1)d_{zz}(2)\frac{1}{r_{12}}s(1)d_{zz}(2)\rangle = \frac{(4\pi)^2}{25}\left\langle\frac{1}{g_{12}}\right\rangle, \quad (16)$$

$$\langle s(1)d_{iz}(2)\frac{1}{r_{12}}d_{iz}(1)s(2)\rangle = \frac{(4\pi)^2}{75}\left\langle\frac{s_{12}^2}{g_{12}^3}\right\rangle, \quad i = x, y \quad (17)$$

$$\langle s(1)d_{zz}(2)\frac{1}{r_{12}}d_{zz}(1)s(2)\rangle = \frac{(4\pi)^2}{25}\left\langle\frac{s_{12}^2}{g_{12}^3}\right\rangle, \quad (18)$$

$$\langle p_i(1)d_{iz}(2)\frac{1}{r_{12}}p_i(1)d_{iz}(2)\rangle = (4\pi)^2\left\langle\frac{1}{45}\frac{1}{g_{12}} + \frac{2}{1575}\frac{s_{12}^2}{g_{12}^3}\right\rangle, \quad i = x, y \quad (19)$$

$$\langle p_z(1)d_{zz}(2)\frac{1}{r_{12}}p_z(1)d_{zz}(2)\rangle = (4\pi)^2\left\langle\frac{1}{25}\frac{1}{g_{12}} - \frac{4}{525}\frac{s_{12}^2}{g_{12}^3}\right\rangle, \quad (20)$$

$$\langle p_i(1)d_{iz}(2)\frac{1}{r_{12}}d_{iz}(1)p_i(2)\rangle = (4\pi)^2\left\langle\frac{1}{225}\frac{s_{12}}{g_{12}^2} + \frac{8}{3675}\frac{s_{12}^3}{g_{12}^4}\right\rangle, \quad i = x, y \quad (21)$$

$$\langle p_z(1)d_{zz}(2)\frac{1}{r_{12}}d_{zz}(1)p_z(2)\rangle = (4\pi)^2\left\langle\frac{1}{225}\frac{s_{12}}{g_{12}^2} - \frac{9}{1225}\frac{s_{12}^3}{g_{12}^4}\right\rangle, \quad (22)$$

$$\langle p_i(1)d_{iz}(2)\frac{1}{r_{12}}p_z(1)d_{zz}(2)\rangle = \frac{(4\pi)^2}{525}\left\langle\frac{s_{12}^2}{g_{12}^3}\right\rangle, \quad i = x, y \quad (23)$$

$$\langle p_i(1)d_{iz}(2)\frac{1}{r_{12}}d_{zz}(1)p_z(2)\rangle = (4\pi)^2\left\langle-\frac{1}{225}\frac{s_{12}}{g_{12}^2} + \frac{4}{1225}\frac{s_{12}^3}{g_{12}^4}\right\rangle, \quad i = x, y \quad (24)$$

$$\langle p_x(1)d_{xz}(2)\frac{1}{r_{12}}p_y(1)d_{yz}(2)\rangle = \frac{(4\pi)^2}{525}\left\langle\frac{s_{12}^2}{g_{12}^3}\right\rangle, \quad (25)$$

$$\langle p_x(1)d_{xz}(2)\frac{1}{r_{12}}d_{yz}(1)p_y(2)\rangle = \frac{(4\pi)^2}{735}\left\langle\frac{s_{12}^3}{g_{12}^4}\right\rangle, \quad (26)$$

$$\langle d_{iz}(1)s(2)\frac{1}{r_{12}}p_i(1)p_z(2)\rangle = \frac{(4\pi)^2}{45}\left\langle\frac{s_{12}}{g_{12}^2}\right\rangle, \quad i = x, y \quad (27)$$

$$\langle d_{iz}(1)p_i(2)\frac{1}{r_{12}}s(1)p_z(2)\rangle = \frac{(4\pi)^2}{75}\left\langle\frac{s_{12}^2}{g_{12}^3}\right\rangle, \quad i = x, y \quad (28)$$

$$\langle p_i(1)d_{iz}(2)\frac{1}{r_{12}}p_z(1)d_{zz}(2)\rangle = \frac{(4\pi)^2}{525}\left\langle\frac{s_{12}^2}{g_{12}^3}\right\rangle, \quad i = x, y \quad (29)$$

$$\langle p_i(1)p_z(2)\frac{1}{r_{12}}s(1)d_{iz}(2)\rangle = \frac{(4\pi)^2}{45}\left\langle\frac{s_{12}}{g_{12}^2}\right\rangle, \quad i = x, y \quad (30)$$

These expressions have been obtained with the help of the algebraic computer program Maple [25].

4.2 Construction of symmetry adapted configurations

The ground state configuration of helium atom in the spectroscopic notation is of the type ss and has S symmetry. We can construct configurations using p -, d - orbitals of S symmetry. These configurations are:

$$\psi_s = ns(1)ns(2) = ss = s^2, \quad (31)$$

$$\psi_p = np(1)np(2) = pp = p^2, \quad (32)$$

$$\psi_p = nd(1)nd(2) = dd = d^2, \quad (33)$$

with

$$\psi_p = pp = p_x(1)p_x(2) + p_y(1)p_y(2) + p_z(1)p_z(2) = p_xp_x + p_y p_y + p_z p_z. \quad (34)$$

The basis functions $p_y p_y$ and $p_z p_z$ may not contribute energetically as much as $p_x p_x$ but they are necessary to have the proper symmetry, so that the wave function is eigenfunction of L^2 . Therefore a matrix element between two of these configurations has to be calculated as:

$$\langle pp | \hat{H} | pp \rangle = \langle p_x p_x + p_y p_y + p_z p_z | H | p_x p_x + p_y p_y + p_z p_z \rangle. \quad (35)$$

One has to note that using symmetry adapted functions or configurations (SAF) and non-SAF the dimensions of the H -matrices are different, whereas a proof of the correctness of the calculation is that the diagonalization of the H -matrices in both cases should lead to the exactly same energy results [20]. We have used the notation pp , but different exponents or powers may be used, pp' .

In the case of d -orbitals:

$$\psi_d = dd = d_{z^2}d_{z^2} + d_{xz}d_{xz} + d_{yz}d_{yz} + d_{xy}d_{xy} + d_{x^2-y^2}d_{x^2-y^2}. \quad (36)$$

5. The use of complex Slater orbitals

The complex Slater orbitals with quantum numbers n, m and l are defined by an unnormalized radial part and an angular orthonormal part which is a spherical harmonic:

$$\begin{aligned}\phi^*(\mathbf{r}) &= r^{n-1}e^{-\alpha r}Y_l^{m*}(\theta, \phi), \\ \phi'(\mathbf{r}) &= r^{n'-1}e^{-\alpha' r}Y_{l'}^{m'}(\theta, \phi).\end{aligned}\tag{37}$$

The spherical harmonics in Condon and Shortley phases [26, p. 52] are given by:

$$Y_l^m(\theta, \phi) = (-1)^m \left[\frac{2l+1}{4\pi} \frac{(l-m)!}{(l+m)!} \right]^{1/2} P_l^m(\cos \theta) e^{im\phi}, \tag{38}$$

where $P_l^m(\cos \theta)$ are the associated Legendre functions. The spherical harmonics and associated Legendre functions used along this work are written explicitly in [27, p. 14].

The charge distributions are:

$$\Omega_{N,L,M}(\mathbf{r}) = \phi^*(\mathbf{r})\phi'(\mathbf{r}) = \sum_{L=|l-l'|}^{l+l'} (2L+1)^{1/2} C^L(l', m'; l, m) r^{N-1} e^{-\omega r} Y_L^M(\theta, \phi), \tag{39}$$

where $N = n + n' - 1$, $M = m' - m$ and the exponents $\omega = \alpha + \alpha'$. N, L, M are the quantum numbers of the charge distributions. $C^L(l', m'; l, m)$ are the Condon and Shortley coefficients [26, p. 52].

5.1 Integrals over complex Slater orbitals

The two-electron integrals appearing in the Hy-CI method are then defined:

$$I(N_1, N_2; \omega_1, \omega_2; \nu)_{l_1, l'_1, l_2, l'_2}^{m_1, m'_1, m_2, m'_2} = \int \Omega_{N_1, L_1, M_1}(\mathbf{r}_1) \Omega_{N_2, L_2, M_2}(\mathbf{r}_2) r_{12}^\nu d\mathbf{r}_1 d\mathbf{r}_2, \tag{40}$$

with the cases $\nu = -1, 0, 1, 2$. After angular integration the two-electron integrals are:

$$\begin{aligned}I(N_1, N_2; \omega_1, \omega_2; \nu)_{l_1, l'_1, l_2, l'_2}^{m_1, m'_1, m_2, m'_2} &= (-1)^{M_1} \delta(M_1 + M_2, 0) \sum_{L_1=|l_1-l'_1|}^{l_1+l'_1} \sum_{L_2=|l_2-l'_2|}^{l_2+l'_2} \delta(L_1, L_2) \\ &\times \prod_{i=1}^2 (2L_i + 1)^{1/2} C^{L_i}(l'_i, m'_i; l_i, m_i) I(N_1, N_2; \omega_1, \omega_2; \nu; L_2)\end{aligned}\tag{41}$$

where $I(N_1, N_2; \omega_1, \omega_2; \nu; L_2)$ are the basic radial two-electron integrals. The occurring basic two-electron integrals in the calculations of helium atom are:

$$I(N_1, N_2; \omega_1, \omega_2; 0; L) = \delta(L, 0) A(N_1 + 1, \omega_1) A(N_2 + 1, \omega_2) \quad (42)$$

$$\begin{aligned} I(N_1, N_2; \omega_1, \omega_2; 1; L) = & \frac{1}{(2L+1)} \\ & \times \left[-\frac{1}{(2L-1)} [V(N_1 + L + 1, N_2 - L + 2; \omega_1, \omega_2) + V(N_2 + L + 1, N_1 - L + 2; \omega_2, \omega_1)] + \right. \\ & \left. + \frac{1}{(2L+3)} [V(N_1 + L + 3, N_2 - L; \omega_1, \omega_2) + V(N_2 + L + 3, N_1 - L; \omega_2, \omega_1)] \right] \quad (43) \end{aligned}$$

$$I(N_1, N_2; \omega_1, \omega_2; -1; L) = \frac{1}{(2L+1)} [V(N_1 + L + 1, N_2 - L; \omega_1, \omega_2) + V(N_2 + L + 1, N_1 - L; \omega_2, \omega_1)]. \quad (44)$$

$$\begin{aligned} I(N_1, N_2; \omega_1, \omega_2; 2; L) = & \delta(L, 0) [A(N_1 + 3, \omega_1) A(N_2 + 1, \omega_2) + A(N_2 + 3, \omega_2) A(N_1 + 1, \omega_1)] \\ & - \frac{2}{3} \delta(L, 1) A(N_1 + 2, \omega_1) A(N_2 + 2, \omega_2) \quad (45) \end{aligned}$$

$A(n, \alpha)$ and $V(k, l; \alpha, \beta)$ are auxiliary two-electron integrals defined in Ref. [29].

5.2 Hylleraas-CI two-electron kinetic energy integrals

In this section we treat the two-electron kinetic energy integrals appearing in the Hy-CI method when using the Hamiltonian in Hylleraas coordinates [23]. For any atomic number $N \geq 3$ the kinetic energy integrals are of two- and three-electron type. The three-electron kinetic energy integrals have been evaluated in Refs. [28, 29]. For $N = 2$ the integrals are of course, of two-electron type. Sims and Hagstrom [28] evaluated the kinetic energy integrals using the transformation of Kolos and Roothaan [30] which partially avoids the differentiation with respect to r_{ij} terms appearing on the right hand side of the matrix elements. In this work we will perform the derivatives directly over r_{ij} and using Hamiltonian written in polar and interelectronic coordinates, we shall prove its correctness and will solve the resulting integrals in terms of basic two-electron integrals defined in Ref. [29].

The Hamiltonian in Hylleraas coordinates can be separated in a sum of one electron potential and kinetic energy operators:

$$\hat{H} = \sum_{i=1}^n \hat{H}(i), \quad \hat{H}(1) = \hat{T}(1) + \hat{V}(1) = \hat{T}_R(1) + \hat{T}_\theta(1) + \hat{V}(1). \quad (46)$$

The the kinetic energy operator can be again separated into radial and angular parts. Let us evaluate the kinetic energy of electron 1:

$$\hat{T}(1) = \hat{T}_{R_1}(1) + \hat{T}_{R_2}(1) + \hat{T}_{R_3}(1) + \hat{T}_L(1) + \hat{T}_{\theta_1}(1) + \hat{T}_{\theta_2}(1) + \hat{T}_{\theta_3}(1). \quad (47)$$

The radial operators are:

$$\hat{T}_{R_1}(1) = -\frac{1}{2} \frac{\partial^2}{\partial r_1^2} - \frac{1}{r_1} \frac{\partial}{\partial r_1}, \quad (48)$$

$$\hat{T}_{R_2}(1) = -\frac{2}{r_{12}} \frac{\partial}{\partial r_{12}}, \quad (49)$$

$$\hat{T}_{R_3}(1) = -\frac{1}{2} \frac{r_1^2 + r_{12}^2 - r_2^2}{r_1 r_{12}} \frac{\partial^2}{\partial r_1 \partial r_{12}}, \quad (50)$$

and the angular ones:

$$\hat{T}_L(1) = \frac{1}{2} \frac{\hat{L}^2}{r_1^2}, \quad \hat{L}^2(1) = -\frac{\partial^2}{\partial \theta_1^2} - \frac{1}{\sin^2 \theta_1} \frac{\partial^2}{\partial \phi_1^2} - \cot \theta_1 \frac{\partial}{\partial \theta_1} \quad (51)$$

$$\hat{T}_{\theta_1}(1) = -\frac{r_2}{r_1 r_{12}} \frac{\cos \theta_2}{\sin \theta_1} \frac{\partial^2}{\partial \theta_1 \partial r_{12}}, \quad (52)$$

$$\hat{T}_{\theta_2}(1) = -\frac{1}{2} \cot \theta_1 \frac{r_{12}^2 - r_1^2 - r_2^2}{r_1^2 r_{12}} \frac{\partial^2}{\partial \theta_1 \partial r_{12}}, \quad (53)$$

$$\hat{T}_{\theta_3}(1) = -\frac{r_2}{r_1 r_{12}} \frac{\sin \theta_2}{\sin \theta_1} \sin(\phi_1 - \phi_2) \frac{\partial^2}{\partial \phi_1 \partial r_{12}}, \quad (54)$$

the potential energy operator is:

$$\hat{V}(1) = -\frac{2}{r_1}, \quad (55)$$

as $Z = 2$ for helium. In two-electron kinetic energy integrals we have basis functions CI type with $\nu = 0$ and basis functions Hy-CI type with $\nu = 1$. In the following, we will use ν for power of r_{12} in the left hand side basis functions and ν' on the right ones. The interelectronic distance in the integral has then the power $r_{12}^{\nu+\nu'}$.

The nuclear attraction potential energy is:

$$\begin{aligned} I_{PE}(1) &= \left\langle \phi(\mathbf{r}_1) \phi(\mathbf{r}_2) r_{12}^\nu | \hat{V} | \phi(\mathbf{r}_1) \phi(\mathbf{r}_2) r_{12}^{\nu'} \right\rangle \\ &= -2I(N_1 - 1, N_2; \omega_1, \omega_2; \nu + \nu')_{l_1, l'_1, l_2, l'_2}^{m_1, m'_1, m_2, m'_2}, \quad \nu, \nu' = 0, 1 \end{aligned} \quad (56)$$

with 2 the atomic nuclear charge.

For the kinetic energy we have to evaluate:

$$I_{KE}(1) = \left\langle \phi(\mathbf{r}_1)\phi(\mathbf{r}_2)r_{12}^\nu |\hat{T}_R + \hat{T}_\theta| \phi(\mathbf{r}_1)\phi(\mathbf{r}_2)r_{12}^{\nu'} \right\rangle \quad (57)$$

The radial part:

$$I_{KE,R} = \left\langle \phi(\mathbf{r}_1)\phi(\mathbf{r}_2)r_{12}^\nu |\hat{T}_{R_1}(1) + \hat{T}_{R_2}(1) + \hat{T}_{R_3}(1)| \phi(\mathbf{r}_1)\phi(\mathbf{r}_2)r_{12}^{\nu'} \right\rangle \quad (58)$$

performing the derivatives given by the operators Eq. (48-50) and using the definition of the two-electron integrals Eq. (40), it can be straightforward obtained:

$$\begin{aligned} I_{KE,R_1} = & -\frac{(n_1'^2 + n_1')}{2} I(N_1 - 2, N_2; \omega_1, \omega_2; \nu + \nu')_{l_1, l_1', l_2, l_2'}^{m_1, m_1', m_2, m_2'} \\ & + (n_1' \alpha_1' + \alpha_1') I(N_1 - 1, N_2; \omega_1, \omega_2; \nu + \nu')_{l_1, l_1', l_2, l_2'}^{m_1, m_1', m_2, m_2'} \\ & - \frac{\alpha_1'^2}{2} I(N_1, N_2; \omega_1, \omega_2; \nu + \nu')_{l_1, l_1', l_2, l_2'}^{m_1, m_1', m_2, m_2'}, \end{aligned} \quad (59)$$

$$\begin{aligned} I_{KE,R_2} = & -\nu' \frac{n_1'}{2} \left[I(N_1, N_2; \omega_1, \omega_2; \nu + \nu' - 2)_{l_1, l_1', l_2, l_2'}^{m_1, m_1', m_2, m_2'} \right. \\ & + I(N_1, N_2 - 2; \omega_1, \omega_2; \nu + \nu')_{l_1, l_1', l_2, l_2'}^{m_1, m_1', m_2, m_2'} \\ & \left. - I(N_1 - 2, N_2 + 2; \omega_1, \omega_2; \nu + \nu' - 2)_{l_1, l_1', l_2, l_2'}^{m_1, m_1', m_2, m_2'} \right] \\ & + \nu' \frac{\alpha_1'}{2} \left[I(N_1 + 1, N_2; \omega_1, \omega_2; \nu + \nu' - 2)_{l_1, l_1', l_2, l_2'}^{m_1, m_1', m_2, m_2'} \right. \\ & + I(N_1 - 1, N_2; \omega_1, \omega_2; \nu + \nu')_{l_1, l_1', l_2, l_2'}^{m_1, m_1', m_2, m_2'} \\ & \left. - I(N_1 - 1, N_2 + 2; \omega_1, \omega_2; \nu + \nu' - 2)_{l_1, l_1', l_2, l_2'}^{m_1, m_1', m_2, m_2'} \right], \end{aligned} \quad (60)$$

$$I_{KE,R_3} = -\nu' I(N_1, N_2 + 2; \omega_1, \omega_2; \nu + \nu' - 2)_{l_1, l_1', l_2, l_2'}^{m_1, m_1', m_2, m_2'}. \quad (61)$$

The factor ν' ensures that CI configurations will not contribute and but the Hy-CI will contribute: $\nu' = 1$. The integral containing the the square of the angular momentum operator can be easily evaluated by means of its eigenvalue equation:

$$\begin{aligned}
I_{KE,\theta_1,L} &= \left\langle \phi(\mathbf{r}_1)\phi(\mathbf{r}_2)r_{12}^\nu \left| \frac{1}{2} \frac{\hat{L}_1^2}{r_1^2} \right| \phi(\mathbf{r}_1)\phi(\mathbf{r}_2)r_{12}^{\nu'} \right\rangle \\
&= \frac{1}{2} l'_1(l'_1 + 1) I(N_1 - 2, N_2; \omega_1, \omega_2; \nu + \nu', L_2)_{l_1, l'_1, l_2, l'_2}^{m_1, m'_1, m_2, m'_2},
\end{aligned} \tag{62}$$

where l'_1 is the quantum number of $\phi(\mathbf{r}_1)$.

The evaluation of the angular kinetic energy is more involving. The following integrals should be evaluated:

$$I_{KE,\theta_1} = - \left\langle \phi(\mathbf{r}_1)\phi(\mathbf{r}_2)r_{12}^\nu \left| \frac{r_2}{r_1 r_{12}} \frac{\cos \theta_2}{\sin \theta_1} \frac{\partial^2}{\partial \theta_1 \partial r_{12}} \right| \phi(\mathbf{r}_1)\phi(\mathbf{r}_2)r_{12}^{\nu'} \right\rangle, \tag{63}$$

$$I_{KE,\theta_2} = - \frac{1}{2} \left\langle \phi(\mathbf{r}_1)\phi(\mathbf{r}_2)r_{12}^\nu \left| \frac{(r_{12}^2 - r_1^2 - r_2^2)}{r_1^2 r_{12}} \cot \theta_1 \frac{\partial^2}{\partial \theta_1 \partial r_{12}} \right| \phi(\mathbf{r}_1)\phi(\mathbf{r}_2)r_{12}^{\nu'} \right\rangle, \tag{64}$$

$$I_{KE,\phi_3} = - \left\langle \phi(\mathbf{r}_1)\phi(\mathbf{r}_2)r_{12}^\nu \left| \frac{r_2}{r_1 r_{12}} \frac{\sin \theta_2}{\sin \theta_1} \sin(\phi_1 - \phi_2) \frac{\partial^2}{\partial \phi_1 \partial r_{12}} \right| \phi(\mathbf{r}_1)\phi(\mathbf{r}_2)r_{12}^{\nu'} \right\rangle. \tag{65}$$

First the derivatives of the spherical harmonics with respect to the polar angle [31, 5.7.] is made:

$$\begin{aligned}
\frac{\partial Y_l^m(\theta_1, \phi_1)}{\partial \theta_1} &= \frac{1}{2} [(l'_1 + m'_1 + 1)(l'_1 - m'_1)]^{1/2} e^{-i\phi_1} Y_{l'_1}^{m'_1+1}(\theta_1, \phi_1) \\
&\quad - \frac{1}{2} [(l'_1 - m'_1 + 1)(l'_1 + m'_1)]^{1/2} e^{i\phi_1} Y_{l'_1}^{m'_1-1}(\theta_1, \phi_1).
\end{aligned} \tag{66}$$

and the cosine recursion relation is used:

$$\begin{aligned}
\cos \theta_2 Y_{l'_2}^{m'_2}(\theta_2, \phi_2) &= \left[\frac{(l'_2 + m'_2)(l'_2 - m'_2)}{(2l'_2 + 1)(2l'_2 - 1)} \right]^{1/2} Y_{l'_2-1}^{m'_2}(\theta_2, \phi_2) \\
&\quad + \left[\frac{(l'_2 + m'_2 + 1)(l'_2 - m'_2 + 1)}{(2l'_2 + 1)(2l'_2 + 3)} \right]^{1/2} Y_{l'_2+1}^{m'_2}(\theta_2, \phi_2),
\end{aligned} \tag{67}$$

then the products of spherical harmonics are linearized obtaining an expression in terms of $Y_{L_1}^{M_1}(\theta_1, \phi_1), Y_{L_2}^{M_2}(\theta_2, \phi_2)$. After a rotation, see Ref. [29, Eq. (22)] $Y_{L_2}^{M_2}(\theta_2, \phi_2)$ leads to $Y_{L_2}^{M_2}(\theta_1, \phi_1)$. Now the spherical harmonics with the same arguments are linearized again in order to avoid singularities when using the recursion relations containing a sine function:

$$Y_{L_1}^{M_1*}(\theta_1, \phi_1) Y_{L_2}^{M_2}(\theta_1, \phi_1) = \sum_{L=|L_1-L_2|}^{L_1+L_2} \left[\frac{2L+1}{4\pi} \right]^{1/2} C^L(L_2, M_2; L_1, M_1) Y_L^M(\theta_1, \phi_1), \tag{68}$$

$C^L(l', m'; l, m)$ are the Condon and Shortley coefficients [26, Eqs. (6-11)]. The recursion relation containing the sine functions requests that $M \neq 0$ [29, 5.7.]:

$$\begin{aligned} \frac{Y_L^M(\theta_1, \phi_1)}{\sin \theta_1} = & -\frac{1}{2M} \left[\frac{(2L+1)}{(2L+3)} \right]^{1/2} [(L-M+2)(L-M+1)]^{1/2} e^{i\phi_1} Y_{L+1}^{M-1}(\theta_1, \phi_1) \\ & + ((L+M+1)(L+M+2))^{1/2} e^{-i\phi_1} Y_{L+1}^{M+1}(\theta_1, \phi_1) , \quad M+1, M-1 \neq 0. \end{aligned} \quad (69)$$

this is fulfill in our case, because $M = M_1 + M_2 + 1$ or $M = M_1 + M_2 - 1$ and $M_1 = -M_2$ due to the form of the symmetry adapted configurations in helium atom. Substituting into Eq. (63) we have:

$$\begin{aligned} I_{KE, \theta_1}(1) = & \sum_{L_1=|l'_1-l_1|}^{l'_1+l_1} {}^{(2)} \left[\frac{2L_1+1}{4\pi} \right]^{1/2} \left\{ \sum_{L_2=|l'_2-1-l_2|}^{l'_2-1+l_2} {}^{(2)} (2L_2+1)^{1/2} \sum_{L=|L_1-L_2|}^{L_1+L_2} {}^{(2)} \left[\frac{2L+1}{2L+3} \right]^{1/2} \right. \\ & \times \left[\frac{(l'_2+m'_2)(l'_2-m'_2)}{(2l'_2-1)(2l'_2+3)} \right]^{1/2} C^{L_2}(l'_2-1, m'_2; l_2, m_2) f(l'_1, m'_1, L_1, L_2, L, M_1, M_2, M) \\ & \times I(N_1-1, N_2+1; \omega_1, \omega_2; \nu+\nu'-2; L_2) \\ & + \sum_{L'_2=|l'_2+1-l_2|}^{l'_2+1+l_2} {}^{(2)} (2L_2+1)^{1/2} \sum_{L'=|L_1-L'_2|}^{L_1+L'_2} {}^{(2)} \left[\frac{2L'+1}{2L'+3} \right]^{1/2} \left[\frac{(l'_2-m'_2+1)(l'_2+m'_2+1)}{(2l'_2+3)} \right]^{1/2} \\ & \times C^{L'_2}(l'_2+1, m'_2; l_2, m_2) f(l'_1, m'_1, L_1, L'_2, L', M_1, M_2, M) I(N_1-1, N_2+1; \omega_1, \omega_2; \nu+\nu'-2; L'_2) \end{aligned} \quad (70)$$

with the factor f is a function of the quantum numbers:

$$\begin{aligned}
& f(l'_1, m'_1, L_1, L_2, L, M_1, M_2, M) = \\
& (-1)^{M_1+1} \frac{1}{2} \frac{1}{M_1 + M_2 + 1} [(l'_1 + m'_1 + 1)(l'_1 - m'_1)]^{1/2} C^{L_1}(l'_1, m'_1 + 1; l_1, m_1) C^L(L_2, M_2; L_1, -M_1 - 1) \\
& \quad \times \left([(L - M_1 - M_2 + 1)(L - M_1 - M_2)]^{1/2} \int_0^\pi \int_0^{2\pi} Y_{L+1}^{M_1+M_2}(\theta_1, \phi_1) \sin \theta_1 d\theta_1 d\phi_1 \right. \\
& \quad \left. + [(L + M_1 + M_2 + 2)(L + M_1 + M_2 + 3)]^{1/2} \int_0^\pi \int_0^{2\pi} Y_{L+1}^{M_1+M_2+2}(\theta_1, \phi_1) e^{-2i\phi_1} \sin \theta_1 d\theta_1 d\phi_1 \right) \\
& - (-1)^{M_1-1} \frac{1}{M_1 + M_2 - 1} \frac{1}{2} [(l'_1 - m'_1 + 1)(l'_1 + m'_1)]^{1/2} C^{L_1}(l'_1, m'_1 - 1; l_1, m_1) C^L(L_2, M_2; L_1, -M_1 + 1) \\
& \quad \times \left([(L - M_1 - M_2 + 3)(L - M_1 - M_2)]^{1/2} \int_0^\pi \int_0^{2\pi} Y_{L+1}^{M_1+M_2-2}(\theta_1, \phi_1) e^{2i\phi_1} \sin \theta_1 d\theta_1 d\phi_1 \right. \\
& \quad \left. + [(L + M_1 + M_2)(L + M_1 + M_2 + 1)]^{1/2} \int_0^\pi \int_0^{2\pi} Y_{L+1}^{M_1+M_2}(\theta_1, \phi_1) \sin \theta_1 d\theta_1 d\phi_1 \right). \quad (71)
\end{aligned}$$

The first kind of integrals over spherical harmonics are:

$$\int_0^\pi \int_0^{2\pi} Y_{L+1}^{M_1+M_2}(\theta_1, \phi_1) \sin \theta_1 d\theta_1 d\phi_1 = \delta(L+1, 0) \delta(M_1 + M_2, 0). \quad (72)$$

The following integrals are evaluated integrating over the associate Legendre functions :

$$\begin{aligned}
\int_0^\pi \int_0^{2\pi} Y_{L+1}^{M_1+M_2+2}(\theta_1, \phi_1) e^{-2i\phi_1} \sin \theta_1 d\theta_1 d\phi_1 &= 2\pi \int_0^\pi P_{L+1}^{M_1+M_2+2}(\cos \theta_1) \sin \theta_1 d\theta_1 \\
\int_0^\pi \int_0^{2\pi} Y_{L+1}^{M_1+M_2-2}(\theta_1, \phi_1) e^{2i\phi_1} \sin \theta_1 d\theta_1 d\phi_1 &= 2\pi \int_0^\pi P_{L+1}^{M_1+M_2-2}(\cos \theta_1) \sin \theta_1 d\theta_1 \quad (73)
\end{aligned}$$

using the algorithm developed by Wong [33]. The overlap integral over Associate Legendre functions is:

$$\begin{aligned}
\int_0^\pi P_{L_1}^{M_1}(\cos \theta) P_{L_2}^{M_2}(\cos \theta) \sin(\theta) d\theta &= \sum_{p_1=0}^{p_1 \max} \sum_{p_2=0}^{p_2 \max} a_{L_1, M_1}^{p_1} a_{L_2, M_2}^{p_2} \\
&\times \frac{\Gamma\left(\frac{1}{2}(L_1 + L_2 - M_1 - M_2 - 2p_1 - 2p_2 + 1)\right) \Gamma\left(\frac{1}{2}(M_1 + M_2 + 2p_1 + 2p_2 + 2)\right)}{\Gamma\left(\frac{1}{2}(L_1 + L_2 + 3)\right)}, \quad (74)
\end{aligned}$$

Γ are Gamma functions. This formula is valid for $0 \leq M_1 \leq L_1$ and $0 \leq M_2 \leq L_2$. If M is negative the formula is used:

$$P_L^{-M}(\cos \theta_1) = (-1)^M \frac{(L-M)!}{(L+M)!} P_L^M(\cos \theta_1). \quad (75)$$

For even $L_1 + L_2 - M_1 - M_2$ the integral vanish. The coefficients are:

$$a_{L,M}^p = \frac{(-1)^p (L+M)!}{2^{M+2p} (M+p)! p! (L-M-2p)!}. \quad (76)$$

To evaluate the second contribution to the angular kinetic energy we proceed as showed above and need the recursion relation [31, 5.7.]:

$$\begin{aligned} -\cot \theta Y_L^M(\theta_1, \phi_1) &= \frac{1}{2M} [(L+M+1)(L-M)]^{1/2} e^{-i\phi_1} Y_L^{M+1}(\theta_1, \phi_1) \\ &+ \frac{1}{2M} [(L-M+1)(L+M)]^{1/2} e^{i\phi_1} Y_L^{M-1}(\theta_1, \phi_1). \end{aligned} \quad (77)$$

obtaining:

$$\begin{aligned} I_{KE, \theta_1, 2} &= \frac{1}{2} \sum_{L_1=|l'_1-l_1|}^{l'_1+l_1} {}^{(2)}(2L_1+1)^{1/2} \sum_{L_2=|l'_2-l_2|}^{l'_2+l_2} {}^{(2)}(2L_1+1)^{1/2} C^{L_2}(l'_2, m'_2; l_2, m_2) \sum_{L=|L_1-L_2|}^{L_1+L_2} \left[\frac{2L+1}{4\pi} \right]^{1/2} \\ &\quad \left[(-1)^{M_1+1} \frac{1}{2} [(l'_1 + m'_1 + 1)(l'_1 - m'_1)]^{1/2} C^{L_1}(l'_1, m'_1 + 1; l_1, m_1) \right. \\ &\quad \left(\frac{1}{2M} [(L+M_1+M_2+2)(L-M_1-M_2-1)]^{1/2} \int_0^\pi \int_0^{2\pi} Y_{L+1}^{M_1+M_2+2}(\theta_1, \phi_1) e^{-2i\phi_1} \sin \theta_1 d\theta_1 d\phi_1 \right. \\ &\quad \left. + \frac{1}{2M} [(L-M_1-M_2)(L+M_1+M_2+1)]^{1/2} \int_0^\pi \int_0^{2\pi} Y_{L+1}^{M_1+M_2}(\theta_1, \phi_1) \sin \theta_1 d\theta_1 d\phi_1 \right) \\ &\quad - (-1)^{M_1-1} \frac{1}{2} [(l'_1 - m'_1 + 1)(l'_1 + m'_1)]^{1/2} C^{L_1}(l'_1, m'_1 - 1; l_1, m_1) \\ &\quad \left(\frac{1}{2M} [(L+M_1+M_2)(L-M_1-M_2+1)]^{1/2} \int_0^\pi \int_0^{2\pi} Y_{L+1}^{M_1+M_2}(\theta_1, \phi_1) \sin \theta_1 d\theta_1 d\phi_1 \right. \\ &\quad \left. + \frac{1}{2M} [(L-M_1-M_2+2)(L+M_1+M_2-1)]^{1/2} \int_0^\pi \int_0^{2\pi} Y_{L+1}^{M_1+M_2-2}(\theta_1, \phi_1) e^{2i\phi_1} \sin \theta_1 d\theta_1 d\phi_1 \right) \Big] \\ &\quad \times [I(N_1-2, N_2; \omega_1, \omega_2; \nu + \nu' - 2; L_2) - I(N_1, N_2; \omega_1, \omega_2; \nu + \nu' - 2; L_2) \\ &\quad - J(N_1-2, N_2+2; \omega_1, \omega_2; \nu + \nu' - 2; L_2)], \end{aligned} \quad (78)$$

The derivative of the spherical harmonic with $m'_1 = 0$ with respect to ϕ_1 vanishes:

$$I_{KE, \phi_1, 3} = 0 \quad (79)$$

In case of $m_1 \neq 0$:

$$\frac{\partial Y_l^m(\theta, \phi)}{\partial \phi} = i m Y_l^m(\theta, \phi). \quad (80)$$

$\sin(\phi_1 - \phi_3)$ can be written in exponential form:

$$\sin(\phi_1 - \phi_3) = \frac{1}{2i} (e^{i\phi_1} e^{-i\phi_3} - e^{-i\phi_1} e^{i\phi_3}) \quad (81)$$

Similarly one obtains:

$$\begin{aligned} I_{KE,\phi_1,3} = & (-1)^{m'_2} \frac{1}{2} \sqrt{\frac{2}{3}} \left[\frac{2l'_1 + 1}{2l'_1 + 3} \right]^{1/2} \times \sum_{L_1=|l'_1+1-l_1|}^{l'_1+1+l_1} {}^{(2)} \sum_{L_2=|l'_2-l_2|}^{l'_2+l_2} {}^{(2)} \sum_{L'_2=|L_2+l'_2|}^{L_2+l'_2} {}^{(2)} (2L_1+1)(2L_2+1)^{1/2} \\ & \times (2L'_2 + 1)^{1/2} \left\{ C^{L_2}(l'_2, m'_2; l_2, m_2) C^{L_2}(1, -1; l_2, m_2) C^{L'_2}(L_2, -m_2 - 1; l'_2, m'_2) \right. \\ & \times [(l'_1 - m'_1 + 2)(l'_1 - m'_1 + 1)]^{1/2} C^{L_1}(l'_1 + 1, m'_1 - 1; l_1, m_1) \\ & \times \int_0^\pi \int_0^{2\pi} Y_{L_1}^{M_1-1}(\theta_1, \phi_1) Y_{L'_2}^{M_2-1}(\theta_1, \phi_1) e^{2i\phi_1} \sin \theta_1 d\theta_1 d\phi_1 \\ & + [(l'_1 + m'_1 + 1)(l'_1 + m'_1 + 2)]^{1/2} C^{L_1}(l'_1 + 1, m'_1 + 1; l_1, m_1) \\ & \times \int_0^\pi \int_0^{2\pi} Y_{L_1}^{M_1+1}(\theta_1, \phi_1) Y_{L'_2}^{M_2-1}(\theta_1, \phi_1) \sin \theta_1 d\theta_1 d\phi_1 \Big) \\ & + C^{L_2}(1, 1; l_2, m_2) C^{L'_2}(L_2, -m_2 + 1; l'_2, m'_2) \\ & \times [(l'_1 - m'_1 + 2)(l'_1 - m'_1 + 1)]^{1/2} C^{L_1}(l'_1 + 1, m'_1 - 1; l_1, m_1) \\ & \times \int_0^\pi \int_0^{2\pi} Y_{L_1}^{M_1-1}(\theta_1, \phi_1) Y_{L'_2}^{M_2+1}(\theta_1, \phi_1) \sin \theta_1 d\theta_1 d\phi_1 \\ & + [(l'_1 + m'_1 + 1)(l'_1 + m'_1 + 2)]^{1/2} C^{L_1}(l'_1 + 1, m'_1 + 1; l_1, m_1) \\ & \times \int_0^\pi \int_0^{2\pi} Y_{L_1}^{M_1+1}(\theta_1, \phi_1) Y_{L'_2}^{M_2+1}(\theta_1, \phi_1) e^{-2i\phi_1} \sin \theta_1 d\theta_1 d\phi_1 \Big) \\ & \times I(N_1 - 1, N_2 + 1; \omega_1, \omega_2; \nu + \nu' - 2; L'_2) \} \quad (82) \end{aligned}$$

The expressions given here, although they look complicated, most of the terms vanish. They are very sensitive to errors.

Especial case $m'_1 = 0$

The above expressions are general. For the case $m'_1 = 0$, one may obtain simpler expressions using shorter recursion relations for the spherical harmonics Eq. (C.9) of [29]. So it can be easily obtained:

$$\begin{aligned}
I_{KE,\theta_1}(1) = & (-1)^{M_2} \delta(M_1 + M_2, 0) \left[\frac{(2l'_1 + 1)(2l'_1 - 1)}{(2l'_3 + 1)} \right]^{1/2} \sum_{L_1=|l'_1-1-l_1|}^{l'_1-1+l_1} {}^{(2)}(2L_1+1)^{1/2} C^{L_1}(l'_1-1, m'_1; l_1, m_1) \\
& \times \left\{ \left[\frac{(l'_2 - m'_2)(l'_2 + m'_2)}{(2l'_2 - 1)} \right]^{1/2} \times \sum_{L_2=|l'_2-1-l_2|}^{l'_2+l_2} {}^{(2)}\delta(L_1, L'_2)(2L_2+1)^{1/2} \right. \\
& \times C^{L_2}(l'_2-1, m'_2; l_2, m_2) I(N_1-1, N_2+1; \omega_1, \omega_2; \nu + \nu' - 2; L_2) \\
& + \left[\frac{(l'_2 - m'_2 + 1)(l'_2 + m'_2 + 1)}{(2l'_2 + 2)} \right]^{1/2} \sum_{L'_2=|l'_2+1-l_2|}^{l'_2+1+l_2} {}^{(2)}(2L_1+1)^{1/2} (2L'_2+1)^{1/2} \delta(L_1, L'_2) \\
& \left. C^{L'_2}(l'_2+1, m'_2; l_2, m_2) I(N_1-1, N_2+1; \omega_1, \omega_2; \nu + \nu' - 2; L'_2) \right\}. \\
& m'_1 = 0, \quad l'_1 = 1, 2 \quad (83)
\end{aligned}$$

and

$$\begin{aligned}
I_{KE,\theta_{1,2}} = & \frac{1}{2} (-1)^{M_1} \delta(M_1 + M_2, 0) \sum_{L_2=|l'_2-l_2|}^{l'_2+l_2} {}^{(2)}(2L_2+1)^{1/2} C^{L_2}(l'_2, m'_2; l_2, m_2) \\
& \times \left\{ (l'_1 - 1) \left[\frac{(2l'_1 + 1)}{(2l'_1 - 3)} \right]^{1/2} \sum_{L_1=|l'_1-2-l_1|}^{l'_1-2+l_1} {}^{(2)}(2L_1+1)^{1/2} \delta(L_1, L_2) C^{L_1}(l'_1-2, m'_1; l_1, m_1) \right. \\
& \quad \left. + l'_1 \sum_{L'_1=|l'_1-l_1|}^{l'_1+l_1} {}^{(2)}(2L'_1+1)^{1/2} \delta(L'_1, L_2) C^{L'_1}(l'_1, m'_1; l_1, m_1) \right\} \\
& \times [I(N_1-2, N_2; \omega_1, \omega_2; \nu + \nu'; L_2)_3; 1, 1; L_2, L_3) - I(N_1, N_2; \omega_1, \omega_2; \nu + \nu' - 2; L_2) \\
& \quad - I(N_1-2, N_2+2; \omega_1, \omega_2; \nu + \nu' - 2; L_2)]. \\
& m'_1 = 0, \quad l'_1 = 1, 2 \quad (84)
\end{aligned}$$

The derivative of the spherical harmonic with $m'_1 = 0$ with respect to ϕ_1 vanishes:

$$I_{KE,\phi_3}(1) = 0 \quad (85)$$

5.3 Construction of symmetry adapted configurations

The configurations ss , pp , dd of S symmetry using complex Slater orbitals are constructed:

$$\psi_p = pp = p_0(1)p_0(2) - p_1(1)p_{-1}(2) - p_{-1}(1)p_1(2) = p_0p_0 - p_1p_{-1} - p_{-1}p_1 \quad (86)$$

the basis functions p_1p_{-1} and $p_{-1}p_1$ are energetically degenerated. A matrix element between two of these configurations has to be calculated as:

$$\langle pp | \hat{H} | pp \rangle = \langle p_0p_0 - p_1p_{-1} - p_{-1}p_1 | \hat{H} | p_0p_0 - p_1p_{-1} - p_{-1}p_1 \rangle \quad (87)$$

The configuration dd of S symmetry is constructed:

$$\psi_d = dd = d_0d_0 - d_1d_{-1} - d_{-1}d_1 + d_2d_{-2} + d_{-2}d_2 \quad (88)$$

the basis functions d_1d_{-1} and $d_{-1}d_1$ are degenerated, also d_2d_{-2} and $d_{-2}d_2$.

6. Calculations

6.1 CI Calculations

In order to test the computer code the s, p, d -calculations of Table II of Weiss [5] were reproduced. The recalculated values are shown in Table 1. The CI codes using real and complex orbitals led to the same energy results. Both codes use quadruple precision, about 30 decimal digits in our computer. The advantage of complex orbitals is that general algorithms can be developed and applied, as the angular integration, and general integral subroutines.

We have tried first the full optimization of the CI wave function. Although the energy results were very satisfactory, this technique had to be abandoned because it become impracticable.

In Table 2 we show a set of optimized exponents. They have been optimized in the field of about 10 configurations. Optimal exponents should be obtained by a generalized optimization procedure in the art made by Gaussian orbitals. We have used single and double, and half basis sets, these last were built up by multiplying the exponents of the single basis by 2 or dividing by 2. The double basis could be used until the exponent with value 20.0, further the quadruple precision was not enough. The half basis could be used only for some functions because linear dependence appeared (too similar exponents).

The first 15 terms of the CI wave function in Table 3 are the same than the ones used by Weiss, they gave a good energy result. We also used the first 10 p -functions of Weiss.

Afterwards new terms are added systemstically. We show here the convergence of the 101-term CI wave function as an example. The convergence pattern of the CI wave function was very discouraging. In Table 4 we show our best results obtained using quadruple precision. They agree with the results of Sims and Hagstrom who used 124*real arithmetic and with the results of Bromley and Mitroy [34] using Laguerre functions. A 668 term CI calculation leads to -2.9027662664 a.u. which is about 1 milihartree accurate. The best calculation up to date and the largest expansion is the one of Sims and Hagstrom which is about 4 microhartree above the exact value.

Therefore we arrive to the same conclusion than Carrol, Silverstone and Metzger [32] and Kutzelnigg and Morgan [7]: "For a two electron atom using conventional CI to achieve microhartree accuracy (they mentioned an accuracy of 20 microhartrees) requires enormous labor and sophistication, and indicates that further improvement in accuracy by brutal force CI would be extremely difficult, if not virtually impossible because of numerical linear dependence problems."

6.2 Hy-CI Calculations

We have taken the wave function of Weiss and have added the same functions containing r_{12} . The exponents were slightly optimized in a field of about 10 functions. The set of exponents of the r_{12} -configurations has been taken different than the purely CI configurations, see Table 1. They are in general slightly larger. In Table 5 a 62-term truncated Hy-CI wave function is shown. One can observe the faster convergence of the wave function leading to a result with 4 decimal digit accurate. Note that the computation time was 130 seconds, although the program code has not been refined to save time.

Extensive calculations are shown in Table 6 using only s -, p - and d -orbitals, *i.e.* $L = 2$, and quantum numbers N up to 16 allowed to obtain the energy -2.90372437683996324137 a.u. with Virial factor 1.999999998787224, a result of nanohartree accuracy.

Conclusions

It has been shown that the CI wave function converges stremely slowly. The use of a set of optimized exponents improves the CI expansion. A shorter configuration expansion

is needed by the Hy-CI wave function to obtain a better result. Nanoharteee accuracy has been achieved using a set of s -, p - and d -orbitals and r_{12} . This result can be improved by using a generalized Hy-CI basis set.

Theoretically, the CI and Hy-CI calculations here presented agree with the ones of Sims and Hagstrom and this confirm the correctness of the Hamiltonian in Hylleraas coordinates and of the kinetic energy integral expressions. The results using the Hy-CI wave function are so promising, that it would be worth while the application of the method to larger systems.

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- [1] C. C. Roothaan and A. W. Weiss, Rev. Mod. Phys. **32**, 194 (1960).
- [2] G. W. F. Drake, Phys. Scripta **T83**, 83 (1999).
- [3] J. S. Sims and S. A. Hagstrom, Int. J. Quantum Chem. **90**, 1600, (2002).
- [4] D. C. Clary, *Hylleraas-type wave functions for atoms and diatomic molecules*, Cambridge, England, 1977.
- [5] A. W. Weiss, Phys. Rev **122**, 1826 (1961).
- [6] R. N. Hill, J. Chem. Phys. **83**, 1173 (1985).
- [7] W. Kutzelnigg and J. D. Morgan III, J. Chem. Phys. **96**, 4484 (1992).
- [8] C. Schwartz, Phys. Rev. **126**, 1015 (1962).
- [9] C. Schwartz, Int. J. Mod. Phys. **E15**, 877 (2006).
- [10] T. Kinoshita, Phys. Rev. **105**, 1490 (1957).
- [11] A. J. Thakkar and T. Koga, Phys. Rev. A, **50**, 854 (1994).
- [12] K. Frankowski, and C. L. Pekeris, Phys. Rev. **146**, 46 (1966).
- [13] J. H. Bartlett, Jr., Phys. Rev. **51**, 661 (1937).
- [14] H. Nakashima and H. Nakatsuji, J. Chem. Phys. **127**, 224104 (2007).
- [15] H. Shull and P.-O. Löwdin, J. Chem. Phys. **30**, 617 (1959).
- [16] C. Green, M. M. Mulder, P. C. Milner, M. N. Lewis, J. W. Woll, E. K. Kolchin, and D. Mace, Phys. Rev. **96**, 319 (1954).
- [17] E. A. Hylleraas, Z. Phys. **54**, 347, (1929).
- [18] J. S. Sims and S. A. Hagstrom, Phys. Rev. A **4**, 908 (1971).
- [19] J. S. Sims and S. A. Hagstrom, J. Chem. Phys. **55**, 4699 (1971).
- [20] J. S. Sims, personal communication.
- [21] M. B. Ruiz, to be published.
- [22] J. S. Sims and S. Hagstrom, J. Chem. Phys. **124**, 094101 (2006).
- [23] M. B. Ruiz, Int. J. Quantum Chem. **101**, 246 (2005).
- [24] M. B. Ruiz, Int. J. Quantum Chem. **101**, 261 (2005).
- [25] MAPLE 9 Release by Waterloo Maple Inc. Copyright 2003.
- [26] E. U. Condon and G. H. Shortley, *The theory of atomic spectra*, Cambridge University Press, Cambridge, 1967.

- [27] R. Stevenson, *Multiplet structure of atoms and molecules*, W. B. Saunders Company, Philadelphia & London, 1965.
- [28] J. S. Sims and S. A. Hagstrom, J. Phys. B: At. Mol. Opt. Phys., **40**, 1575 (2007).
- [29] M. B. Ruiz, J. Math. Chem., Online First (2008).
- [30] W. Kolos and C. C. Roothaan, Rev. Mod. Phys. **32**, 219 (1960).
- [31] D. A. Varshalovich, A. N. Moskalev, and V. K. Khersonskii, *Quantum Theory of Angular Momentum*, World Scientific, Singapore (1988).
- [32] D. P. Carrol, H. J. Silverstone, and R. M. Metzger, J. Chem. Phys. **71**, 4142 (1979).
- [33] B. R. Wong, J. Phys. A: Math. Gen. **31**, 1101 (1998).
- [34] M. W. J. Bromley and J. Mitroy, Int. J. Quantum Chem. **107**, 1150 (2007).
- [35] As the Hy-CI wave function consists on only one r_{ij} per configuration and treating now helium atom with only two electrons, the terms of the Hamiltonian including $\frac{\partial^2}{\partial r_{12}^2}$ and $\frac{\partial^2}{\partial r_{12} \partial r_{12}}$ vanish.
- [36] The symmetry of the two-electron integrals should be taken into account. We write here only one case for each.

Table 1: Repetition Weiss calculations [5].

	Confs.	E (a.u.)				Virial
Weiss	15	-2.8789	5525	8604	1.999	999
Weiss	25	-2.9003	9002	0339	1.958	324
Weiss	31	-2.9025	8300	1014	2.000	020

Table 2: Basis set used in the CI and in Hy-CI calculations.

Orbital	CI single	CI double	CI half	Hy-CI single
1s	1.48	2.96	0.74	1.9
2s	1.48	2.96	0.74	1.9
1s'	3.7			3.9
2s'	3.7			3.4
3s	3.7	7.4	1.85	3.0
4s	4.7	9.4	2.35	5.4
5s	5.7	11.4	2.85	4.4
6s	6.7	13.4	3.35	5.5
7s	7.7	15.4	3.85	8.4
8s	8.7	17.4	4.35	8.8
9s	9.7	19.4	4.85	9.8
10s	10.7	20.0	5.35	
11s	11.7	20.0	5.85	
12s	12.7	20.0	6.35	
13s	13.7	20.0	6.85	
14s	14.7	20.0		
15s	15.7	20.0		
2p	2.7	5.4		3.0
3p	2.7	5.4		2.0
2p'	5.4			5.0
3p'	5.4			6.0
4p	3.3	6.6		3.8
5p	3.7	7.4		4.5
6p	4.3	8.6		5.2
7p	4.7	9.4		5.9
8p	5.3	10.6		6.5
9p	5.7	11.4		7.2
10p	6.0	12.0		8.0
11p	6.3	12.6		8.7
12p	6.7	14.0		9.4
13p	7.0	14.6		10.2
14p	7.3			11.0
15p	7.7			11.6
16p	8.0			12.4
3d	3.6	7.2		3.8
4d	2.6	5.2		4.2
5d	4.7	9.4		4.6
6d	5.5	11.0		3.9
7d	6.3	12.6		4.1
8d	7.1	14.2		4.6
9d	7.8	15.6		5.7
10d	8.6	17.2		6.4
11d	9.4	18.8		7.0
12d	10.0	20.0		7.6
13d	10.6	21.2		8.1
14d	11.4			8.6
15d	12.2			9.1
16d	13.0			9.6

Table 3: s -, p - and d - CI calculation on helium atom, 101 terms truncated wave function

expansion.			
N Configuration		Energy	virial Difference
1	1s1s	-2.8046 0000 0000	2.28041
2	1s2s	-2.8464 5649 2449	2.01265 -0.041856492449
3	2s2s	-2.8528 0522 2663	2.03876 -0.006348730214
4	1s1s'	-2.8749 7028 4519	2.00204 -0.022165061856
5	2s1s'	-2.8753 1452 7730	2.00131 -0.000344243211
6	1s'1s'	-2.8762 1971 7811	2.00040 -0.000905190081
7	1s2s'	-2.8774 6546 4594	2.00105 -0.001245746783
8	2s2s'	-2.8784 4308 9302	2.00006 -0.000977624708
9	1s'2s'	-2.8784 9065 1589	2.00005 -0.000047562287
10	2s'2s'	-2.8787 4806 7776	1.99986 -0.000257416187
11	1s3s	-2.8787 8660 6389	2.00004 -0.000038538613
12	2s3s	-2.8788 2609 4249	2.00009 -0.000039487860
13	1s'3s	-2.8789 0234 0012	2.00003 -0.000076245763
14	2s'3s	-2.8789 0276 7328	2.00002 -0.000000427316
15	3s3s	-2.8789 5525 8604	2.00000 -0.000052491276
16	1s4s	-2.8789 5642 2107	2.00000 -0.000001163503
17	2s4s	-2.8789 5663 3396	2.00000 -0.000000211289
18	3s4s	-2.8789 5751 9018	2.00000 -0.000000885622
19	4s4s	-2.8789 7440 1997	1.99999 -0.000016882979
20	1s5s	-2.8789 7575 8637	1.99999 -0.000001356640
21	2s5s	-2.8789 7576 2491	1.99999 -0.000000003854
22	3s5s	-2.8789 7720 3435	1.99999 -0.000001440944
23	4s5s	-2.8789 8084 9335	1.99999 -0.000003645900
24	5s5s	-2.8789 8702 4993	1.99998 -0.000006175658
25	1s6s	-2.8789 8769 6621	1.99998 -0.000000671628
26	2s6s	-2.8789 8772 2861	1.99998 -0.000000026240
27	3s6s	-2.8789 8826 1084	1.99998 -0.000000538223
28	4s6s	-2.8789 8868 8728	1.99998 -0.000000427644
29	5s6s	-2.8789 8975 9206	1.99998 -0.000001070478
30	6s6s	-2.8789 9115 9605	1.99998 -0.000001400399
31	1s7s	-2.8789 9262 2222	1.99999 -0.000001462617
32	2s7s	-2.8789 9262 9635	1.99999 -0.000000007413
33	3s7s	-2.8789 9327 4255	1.99998 -0.000000644620
34	4s7s	-2.8789 9335 5895	1.99999 -0.000000081640
35	5s7s	-2.8789 9346 3799	1.99998 -0.000000107904
36	6s7s	-2.8789 9377 7455	1.99998 -0.000000313656
37	7s7s	-2.8789 9419 5042	1.99998 -0.000000417587
38	1s8s	-2.8789 9565 2668	1.99999 -0.000001457626
39	2s8s	-2.8789 9565 4581	1.99999 -0.000000001913
40	3s8s	-2.8789 9600 4814	1.99999 -0.000000350233
41	4s8s	-2.8789 9606 3092	1.99999 -0.000000058278
42	5s8s	-2.8789 9608 4638	1.99999 -0.000000021546
43	6s8s	-2.8789 9611 7732	1.99999 -0.000000033094
44	7s8s	-2.8789 9624 1954	1.99999 -0.000000124222
45	8s8s	-2.8789 9639 3931	1.99999 -0.000000151977
46	2p2p	-2.8980 1066 3847	1.99720 -0.019014269916
47	2p3p	-2.8983 0353 5068	1.99927 -0.000292871213
48	3p3p	-2.8999 8445 0188	2.00053 -0.001680915128

Continuation Table 3.

N	Configuration	Energy	virial	Difference
49	2p2p'	-2.9000 1939 5255	2.00040	-0.000034945067
50	3p2p'	-2.9000 2572 8711	2.00030	-0.000006333456
51	2p'2p'	-2.9003 0029 7330	2.00012	-0.000274568619
52	2p3p'	-2.9003 0993 6342	2.00014	-0.000009639012
53	3p3p'	-2.9003 4614 9487	2.00001	-0.000036213145
54	2p'3p'	-2.9003 4931 2787	2.00002	-0.000003163300
55	3p'3p'	-2.9004 2459 8409	2.00001	-0.000075285622
56	2p4p	-2.9004 3166 9931	2.00003	-0.000007071522
57	3p4p	-2.9004 3221 0413	2.00004	-0.000000540482
58	4p4p	-2.9004 3399 3582	2.00004	-0.000001783169
59	2p5p	-2.9004 3400 6808	2.00004	-0.000000013226
60	3p5p	-2.9004 3508 9064	2.00005	-0.000001082256
61	4p5p	-2.9004 4229 5990	2.00002	-0.000007206926
62	5p5p	-2.9004 4249 5331	2.00002	-0.000000199341
63	2p6p	-2.9004 4266 5968	2.00002	-0.000000170637
64	3p6p	-2.9004 4268 0235	2.00002	-0.000000014267
65	4p6p	-2.9004 4712 1025	2.00002	-0.000004440790
66	5p6p	-2.9004 5007 1856	2.00003	-0.000002950831
67	6p6p	-2.9004 5688 7282	2.00002	-0.000006815426
68	2p7p	-2.9004 5688 7957	2.00002	-0.000000000675
69	3p7p	-2.9004 5691 7483	2.00002	-0.000000029526
70	4p7p	-2.9004 6603 9818	2.00001	-0.000009122335
71	5p7p	-2.9004 6617 5403	2.00001	-0.000000135585
72	6p7p	-2.9004 6618 6237	2.00001	-0.000000010834
73	7p7p	-2.9004 7220 2637	2.00001	-0.000006016400
74	2p8p	-2.9004 7221 0819	2.00001	-0.000000008182
75	3p8p	-2.9004 7221 5238	2.00001	-0.000000004419
76	4p8p	-2.9004 7250 5447	2.00001	-0.000000290209
77	5p8p	-2.9004 7255 4026	2.00001	-0.000000048579
78	6p8p	-2.9004 7428 5314	2.00001	-0.000001731288
79	7p8p	-2.9004 7683 0335	2.00001	-0.000002545021
80	8p8p	-2.9004 7916 7253	2.00001	-0.000002336918
81	3d3d	-2.9020 6435 2165	1.99950	-0.001585184912
82	3d4d	-2.9021 5865 5625	1.99974	-0.000094303460
83	4d4d	-2.9025 6734 4690	1.99988	-0.000408689065
84	3d5d	-2.9025 7143 9942	1.99990	-0.000004095252
85	4d5d	-2.9025 7753 1336	1.99995	-0.000006091394
86	5d5d	-2.9026 6778 7092	2.00001	-0.000090255756
87	3d6d	-2.9026 7329 8893	2.00002	-0.000005511801
88	4d6d	-2.9026 7446 9528	2.00002	-0.000001170635
89	5d6d	-2.9026 7512 9159	2.00001	-0.000000659631
90	6d6d	-2.9026 9774 0952	2.00002	-0.000022611793
91	3d7d	-2.9026 9775 3228	2.00002	-0.000000012276
92	4d7d	-2.9027 0076 2033	2.00003	-0.000003008805
93	5d7d	-2.9027 0111 8387	2.00003	-0.000000356354
94	6d7d	-2.9027 0375 0417	2.00002	-0.000002632030
95	7d7d	-2.9027 1095 2280	2.00002	-0.000007201863

Continuation Table 3.				
N Configuration		Energy		virial Difference
96	3d8d	-2.9027 1106 4338	2.00002	-0.000000112058
97	4d8d	-2.9027 1112 0091	2.00002	-0.000000055753
98	5d8d	-2.9027 1223 1094	2.00002	-0.000001111003
99	6d8d	-2.9027 1244 9861	2.00002	-0.000000218767
100	7d8d	-2.9027 1499 4392	2.00002	-0.000002544531
101	8d8d	-2.9027 1789 6028	2.00002	-0.000002901636
Exact		-2.9037 2443 1992		-0.001006535964

Calculation time 537 seconds.

Table 4: Comparison of extensive spd-CI calculations on helium atom.

L_{\max}	N_{\max}	Confs.	This work	N_{\max}	Confs.	Sims and Hagstrom [3]	N_{orb}	Bromley and Mitroy [34]
0	15	296	-2.879 028 6809	21	470	-2.879 028 7565	44	-2.879 028 760
1	16	497	-2.900 515 8544	21	854	-2.900 516 2199	80	-2.900 516 228
2	16	668	-2.902 766 2664	21	1221	-2.902 766 8053	115	-2.902 766 823
Best CI	18	15			4699	-2.903 720 091 9	465	-2.903 712 786

In this work were used the exponents of Table 1. Sims and Hagstrom used 4.10 and 25.0 for s -orbitals,

3.05 and 40.5 for p -orbitals and 3.50 and 40.5 for d -orbitals.

Bromley and Mitroy used Laguerre functions with the exponent 8.6 for s -orbitals, 11.6 for p -orbitals and 14.4 for d -orbitals. N_{orb} is the number of orbitals.

Table 5: s-,p- and d- Hy-CI calculation on helium atom with optimization of the orbital

exponents from Table 1.

N Configuration	Energy	virial	Difference
1 1s1s	-2.8046 0000 0000 0000 0000 2.280405		
2 1s2s	-2.8464 5649 2448 7886 8848 2.012655 -0.041856492449		
3 2s2s	-2.8528 0522 2662 7660 6893 2.038758 -0.006348730214		
4 1s1s'	-2.8749 7028 4518 6921 8631 2.002043 -0.022165061856		
5 2s1s'	-2.8753 1452 7730 4383 9933 2.001306 -0.000344243212		
6 1s'1s'	-2.8762 1971 7810 5121 5735 2.000400 -0.000905190080		
7 1s2s'	-2.8774 6546 4594 0870 3077 2.001049 -0.001245746784		
8 2s2s'	-2.8784 4308 9302 1401 8945 2.000063 -0.000977624708		
9 1s'2s'	-2.8784 9065 1588 5673 6622 2.000045 -0.000047562286		
10 2s'2s'	-2.8787 4806 7775 6347 2228 1.999859 -0.000257416187		
11 1s3s	-2.8787 8660 6389 3286 6871 2.000036 -0.000038538614		
12 2s3s	-2.8788 2609 4249 0916 2944 2.000087 -0.000039487860		
13 1s'3s	-2.8789 0234 0012 1737 8000 2.000025 -0.000076245763		
14 2s'3s	-2.8789 0276 7327 8845 3632 2.000022 -0.000000427316		
15 3s3s	-2.8789 5525 8603 6072 3426 1.999999 -0.000052491276		
16 1s1sr ₁₂	-2.9030 3855 5047 6765 9888 2.000060 -0.024083296444		
17 1s2sr ₁₂	-2.9030 3963 0490 7037 1147 1.999905 -0.000001075443		
18 2s2sr ₁₂	-2.9032 5861 2556 4860 4038 2.000030 -0.000218982066		
19 1s1s'r ₁₂	-2.9033 8299 6275 5132 6846 2.000091 -0.000124383719		
20 2s1s'r ₁₂	-2.9034 1178 0236 9870 1758 2.000012 -0.000028783961		
21 1s'1s'r ₁₂	-2.9034 3722 4940 8831 4415 1.999989 -0.000025444704		
22 1s2s'r ₁₂	-2.9034 3950 8142 1374 1002 1.999972 -0.000002283201		
23 2s2s'r ₁₂	-2.9034 6815 0498 5144 6232 1.999956 -0.000028642356		
24 1s'2s'r ₁₂	-2.9034 6820 5099 9614 1845 1.999956 -0.000000054601		
25 2s'2s'r ₁₂	-2.9034 7311 4551 4696 4381 1.999952 -0.000004909451		
26 1s3sr ₁₂	-2.9034 7648 8273 0412 1726 1.999992 -0.000003373722		
27 2s3sr ₁₂	-2.9034 7957 2554 5670 0172 2.000002 -0.000003084282		
28 1s'3sr ₁₂	-2.9034 8135 6723 1881 1971 2.000003 -0.000001784169		
29 2s'3sr ₁₂	-2.9034 8172 3768 1817 9421 2.000002 -0.000000367045		
30 3s3sr ₁₂	-2.9034 8191 0228 3344 9701 2.000003 -0.000000186460		
31 2p2p	-2.9036 9490 9181 3235 6472 1.999946 -0.000212998953		
32 2p3p	-2.9037 0333 9014 5345 8498 1.999973 -0.000008429833		
33 3p3p	-2.9037 1382 9571 8228 7221 1.999986 -0.000010490557		
34 2p2p'	-2.9037 1407 2375 9450 1950 1.999985 -0.000000242804		
35 3p2p'	-2.9037 1429 5379 2885 5478 1.999989 -0.000000223003		
36 2p'2p'	-2.9037 1572 6120 9390 5519 1.999990 -0.000001430742		
37 2p3p'	-2.9037 1588 5177 7166 9859 1.999993 -0.000000159057		
38 3p3p'	-2.9037 1634 2690 0297 1140 1.999994 -0.000000457512		
39 2p'3p'	-2.9037 1644 9779 9809 6406 1.999993 -0.000000107090		
40 3p'3p'	-2.9037 1644 9785 9439 7737 1.999993 -0.000000000006		

Continuation Table 5.

N	Configuration	Energy	virial	Difference
41	$2p2pr_{12}$	-2.9037 2173 2417 9137 9221	1.999989	-0.000005282632
42	$2p3pr_{12}$	-2.9037 2182 0699 2263 4691	1.999990	-0.000000088281
43	$3p3pr_{12}$	-2.9037 2214 9854 2463 6331	1.999993	-0.000000329155
44	$2p2p'r_{12}$	-2.9037 2227 8371 0330 7986	1.999994	-0.000000128517
45	$3p2p'r_{12}$	-2.9037 2237 5963 4585 9805	1.999994	-0.000000097592
46	$2p'2p'r_{12}$	-2.9037 2265 5745 0023 6384	1.999994	-0.000000279782
47	$2p3p'r_{12}$	-2.9037 2272 5043 9425 8433	1.999994	-0.000000069299
48	$3p3p'r_{12}$	-2.9037 2278 0206 3073 0904	1.999995	-0.000000055162
49	$2p'3p'r_{12}$	-2.9037 2287 1724 9868 5604	1.999996	-0.000000091519
50	$3p'3p'r_{12}$	-2.9037 2311 0207 5489 3605	1.999997	-0.000000238483
51	$3d3d$	-2.9037 2311 5896 1644 4399	1.999997	-0.000000005689
52	$3d4d$	-2.9037 2325 3694 3809 8700	1.999996	-0.000000137798
53	$4d4d$	-2.9037 2341 0977 7800 8564	1.999997	-0.000000157283
54	$3d5d$	-2.9037 2363 2223 7418 5292	1.999998	-0.000000221246
55	$4d5d$	-2.9037 2368 3956 6486 0703	1.999998	-0.000000051733
56	$5d5d$	-2.9037 2371 6568 3659 1072	1.999999	-0.000000032612
57	$3d3dr_{12}$	-2.9037 2375 1435 0361 1170	1.999999	-0.000000034867
58	$3d4dr_{12}$	-2.9037 2375 1898 7744 7923	1.999999	-0.000000000464
59	$4d4dr_{12}$	-2.9037 2376 3066 1777 0715	1.999999	-0.000000011167
60	$3d5dr_{12}$	-2.9037 2377 6768 3902 6301	1.999999	-0.000000013702
61	$4d5dr_{12}$	-2.9037 2377 8464 9764 7830	1.999999	-0.000000001697
62	$5d5dr_{12}$	-2.9037 2378 4817 0105 8051	1.999999	-0.000000006352
Exact		-2.9037 2437 7034 1195 9831		-0.000000592217

Calculation time: 130 seconds. 0.5 microhartree accuracy.

Table 6: Comparison of extensive Hy-CI calculations on helium atom using single basis set.

L_{\max}	N_{\max}	Confs.	This work	Accuracy
0	15	378	-2.9034 9813 4711 9664 5493	milihartree
1	16	482	-2.9037 2426 1717 2135 6263	microhartree
2	16	692	-2.9037 2437 6839 9632 4137	nanohartree
Exact			-2.9037 2437 7034 1195 9831 12	

These values are obtained in QP. In this work the exponents of Table 1 were used.